

SPECTRAL ANALYSIS OF Sm^{3+} AND Dy^{3+} IONS DOPED CADMIUM LEAD BORO ALUMINIUM FLUORIDE GLASSES

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Abstract : Photoluminescence properties of cadmium lead boro aluminium fluoride (CdPbBAIF) glasses doped with Sm^{3+} and Dy^{3+} ions as a function of various doping concentrations have been synthesized by melt quenching technique. Moreover, the spectroscopic properties of the prepared glasses have been studied by Fourier transform infrared spectroscopy (FTIR), optical absorption analysis, photoluminescence excitation (PLE) and Photoluminescence (PL) analysis. The emission spectra of Sm^{3+} : CdPbBAIF glasses have shown an intense orange-red emission and Dy^{3+} : CdPbBAIF glasses exhibited yellow emission with the excitation at 402 nm and 385 nm respectively. The luminescence quenching behavior of the prepared glasses as a function of the doping molar concentration of Sm^{3+} and Dy^{3+} ions was analyzed, which could be useful for optimizing the potential composition towards the novel optical applications. Energy level diagram representing the emission lines and decay curves of the prominent emission transitions of the glasses have been presented.

IndexTerms - Spectral analysis; CdPbBAIF glasses; Sm^{3+} and Dy^{3+} ions; Photoluminescence properties; emission; excitation

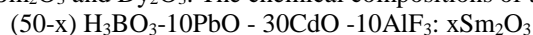
I. INTRODUCTION

Recently, rare-earth ions doped inorganic glasses, ceramics or phosphors are considerably significant due to their high chemical stability and high luminescence efficiency. From the literature it is known that, compared to the ceramics and phosphors, glasses are considered as the excellent host materials because of their features such as good mechanical, chemical and thermal stability, flexibility to add rare earth ions in different concentrations, easy preparation, possibility of obtaining bulk samples and the low cost. Besides the properties, the preparation of rare earth ions doped glasses has also gripped the researchers with their applications in different fields such as solid state lasers, light converters, sensors, channel waveguides, infrared to visible up-converters, field emission displays and optical fiber amplifiers for optical communications, optoelectronics and magento optical devices [1-8]. We have earlier reported on the preparation and the optical characterization of different glasses based on tellurites, phosphates, borates [9–14]. In the present work, as the host we have chosen the inorganic luminescent combination of boro and aluminium fluoride glasses to study the luminescence performance with respect to the dopant concentration. In this combination of cadmium lead boro aluminum fluoride glasses, B_2O_3 could be found as a network former (NWF) and the other oxides such as CdO, PbO and AlF_3 are used as the network modifiers (NWM) when those were added to the B_2O_3 based structure which can boost up certain electrical, chemical, thermal and optical properties [15]. With these enhanced properties due to network modifiers such as PbO and AlF_3 , these synthesized glasses were considered as the capable materials for various optical applications [14]. These glasses have good optical quality and are stable against atmospheric moisture [15]. Rare-earth ions doped phosphate glasses with various visible emissions are useful in developing new light sources, display devices, UV-sensors and tunable visible lasers [16-19]. One of the most important concerns in rare earth doped glasses is to define the dopant environment. Hypersensitive transitions are observed in the spectra of all rare earth ions having more than one f electron. Hypersensitive transitions of rare earth ions manifest as anomalous sensitivity of line strength to the character of the dopant environment [20, 21]. Sm^{3+} is one of the significant rare earth ion due to its increasing demand in various fluorescent devices, high density optical storage, under sea communication, color display and visible solid-state lasers due to its bright emission in orange or red regions [22, 23]. The $^4\text{G}_{5/2}$ level of Sm^{3+} exhibits relatively high quantum efficiency and shows various populating and quenching emission channels resulting interesting fluorescence properties [24]. Dy^{3+} ($4f^9$) ion is the best choice for developing the full colour optical display systems. The analysis of luminescence from the $^4\text{F}_{9/2}$ level of Dy^{3+} ions is very interesting as it ranges in the visible and NIR regions. Limited attention has been paid to the visible emission originating from the $^4\text{F}_{9/2}$ state because of the complicated electronic structure of the $4f^9$ configuration of Dy^{3+} ions and the large number of energy levels lying close to each other makes the interpretation of the spectra cumbersome [25-30].

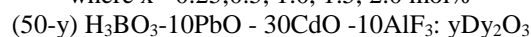
In this article, our aim is to study the emission properties for different concentrations of Sm^{3+} and Dy^{3+} ions doped CdPbBAIF glasses and observe the luminescence quenching behavior of the prepared glasses as a function of the activator molar concentration to evaluate the potential glass among different concentrations of Sm^{3+} and Dy^{3+} : CdPbBAIF glasses for novel optical applications.

II EXPERIMENTAL STUDIES

Sm³⁺ and Dy³⁺: CdPbBAIF glasses were prepared by the melt quenching method. The starting chemicals used were reagent grade of H₃BO₃, Al₂F₃, PbO, CdO, Sm₂O₃ and Dy₂O₃. The chemical compositions of the prepared glasses are as follows:



where $x = 0.25, 0.5, 1.0, 1.5, 2.0$ mol%



where $y = 0.25, 0.5, 1.0, 1.5, 2.0$ mol%

For our convenience, the compositions above are labelled as Sm³⁺ and Dy³⁺: CdPbBAIF glasses. The chemicals were thoroughly mixed in an agate mortar, using a pestle. The obtained homogeneous mixture was taken into an alumina crucible and heated up to 1000°C in an electrical furnace for 2 hours in order to obtain a homogenous melt. Thereafter, the melt was poured into a pre-heated brass mould, and the same was kept in an annealing furnace at a temperature of 400°C about 6 h. This was done in order to remove the thermal stresses and internal strains near the grain boundaries of the prepared glasses. Thereafter, the obtained glasses were polished so that their physical and optical properties could be measured. The UV-Vis-NIR absorption measurements were carried out using a JASCO-V 670 UV-VIS-NIR spectrophotometer and the PLE and PL spectra were recorded using a Jobin Yvon Fluorolog - 3 fluoro - meter, with a Xenon flash lamp as an excitation source. All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

3.1. Sm³⁺: CdPbBAIF glasses

The absorption spectrum (Vis-NIR) of Sm³⁺ glass is shown in Fig. 1. All the transitions in absorption spectrum start from the ground state ⁶H_{5/2} to the various excited states. The transitions observed in the spectrum are intra configuration (f-f) transition. The observed eight absorption bands are centered at 1076 nm, 1225 nm, 1375 nm, 1473 nm are assigned to ⁴G_{5/2}, ⁶F_{11/2}, ⁶F_{9/2}, ⁶F_{7/2}, ⁶F_{5/2}, ⁶F_{3/2} and ⁶F_{1/2} energy levels respectively [31]. The excitation spectrum of Sm³⁺: glass is shown in Fig.2. From this, five excitation bands are identified in the visible region at 404 nm, 417 nm, 443 nm, 478 nm, and 525 nm which are assigned to the electronic transitions (⁶H_{5/2} → ⁴F_{7/2}), [⁶H_{5/2} → (⁶P, ⁴P)_{5/2}], (⁶H_{5/2} → ⁴G_{9/2}), (⁶H_{5/2} → ⁴I_{11/2}) and (⁶H_{5/2} → ⁴F_{3/2}) respectively. Sm³⁺: glass exhibits several overlapped excitation bands from 450 to 490 nm wavelength due to its several closely spaced energy levels. When ⁴F_{7/2} (1231 nm) of Sm³⁺ ion is excited, the initial population relaxes finally to ⁴G_{5/2} level. Between ⁴F_{7/2} and ⁴G_{5/2} levels, there are several levels with smaller energy difference, which encourage there efficient non-radiative leading population of ⁴G_{5/2} state. Among these five, the prominent excitation band at 404 nm is selected for the measurement of emission spectra of Sm³⁺: glasses. The emission spectrum of Sm³⁺: glass is shown in Fig. 3. It exhibits four emission transitions at 564 nm (⁴G_{5/2} → ⁶H_{5/2}), 600 nm (⁴G_{5/2} → ⁶H_{7/2}), 647 nm (⁴G_{5/2} → ⁶H_{9/2}) and 705 nm (⁴G_{5/2} → ⁶H_{11/2}). Among these four emission bands, the transition (⁴G_{5/2} → ⁶H_{7/2}) at 598 nm has shown a strong emission [32-34]. The Sm³⁺: glass shows a bright reddish-orange emission when placed under an UV source. The transitions (⁴G_{5/2} → ⁶H_{7/2}) and (⁴G_{5/2} → ⁶H_{9/2}) are allowed magnetic dipole (MD) transitions but the transition (⁴G_{5/2} → ⁶H_{7/2}) is also an electric dipole dominated. The transition (⁴G_{5/2} → ⁶H_{5/2}) is purely an electric dipole (ED) transition [35, 36] The intensity ratio between ED and MD transitions is used to measure the symmetry of the local environment of the trivalent 4f ions. The greater the intensity ratio more is the asymmetry nature [37]. In the present work, the ED transition (⁴G_{5/2} → ⁶H_{7/2}) of Sm³⁺ ion is more intense than the MD transition (⁴G_{5/2} → ⁶H_{5/2}) which specifies the asymmetric nature of the glass host. The energy level diagram for the emission process with $\lambda_{\text{exi}} = 404$ nm in Sm³⁺: glass is shown in Fig 4. The decay curve of the emission transition of 1.5 mol % of Eu³⁺: CdPbBAIF glass at 600 nm along with their life time is shown in the Fig.5. The decay curve is fitted to single exponential function as: $I = K \exp(-t/\tau)$ where 'K' is the constant and value of ' τ ' is decay time of Sm³⁺: CdPbBAIF glass. The obtained life time value is 0.86265 ms.

3.2. Dy³⁺: CdPbBAIF glasses

The absorption spectrum (Vis-NIR) of Dy³⁺: glass is shown in Fig.6. It has strong absorption band in the NIR region. All the transitions in this spectrum start from the ground state ⁶H_{15/2} to the various excited states. The observed absorption bands are centered at 795 nm, 892 nm, 1090nm, 1269nm and 1670 nm are assigned to ⁶F_{3/2}, ⁶F_{5/2}, ⁶F_{7/2}, (⁶H_{7/2}, ⁶F_{9/2}), (⁶F_{11/2}, ⁶H_{9/2}) and ⁶H_{11/2} energy levels respectively are well resolved [38]. In rare- earth ions, the intensity is found to be very sensitive to the environment around the ion. Such transitions are termed as hypersensitive transitions. All the known hypersensitive transitions obey the rule $|\Delta S| = 0, |\Delta L| \leq 2, |\Delta J| \leq 2$ [39]. In the case of Dy³⁺ ion (4f⁹), the hypersensitive (⁶F_{11/2}, ⁶H_{9/2}) is found to be more intense than other transitions. The excitation spectrum of Dy³⁺: glass is shown in Fig. 7. which was measured by monitoring an intense emission wavelength at 482 nm. From this figure, six prominent excitation peaks are identified at 323 nm, 350 nm 364 nm, 387 nm, 426 nm and 453 nm which are assigned to the electronic transitions [⁶H_{15/2} → (⁴M, ⁴I_{5/2})], (⁶H_{15/2} → ⁴I_{11/2}), [⁶H_{15/2} → (⁴I_{13/2}, ⁴F_{7/2})], (⁶H_{15/2} → ⁴G_{11/2}), (⁶H_{15/2} → ⁴I_{15/2}) and (⁶H_{15/2} → ⁴F_{9/2}) respectively based on the energy levels reported earlier [40]. From these excitation transitions, only one prominent transition (⁶H_{15/2} → ⁴I_{15/2}) at 483 nm is selected for the measurement of emission spectrum of Dy³⁺: glasses. The emission spectrum of Dy³⁺: glasses are shown in Fig.8. It shows three emission transitions at 483 nm (⁴F_{9/2} → ⁶H_{15/2}), 575nm (⁴F_{9/2} → ⁶H_{13/2}) and 664nm (⁴F_{9/2} → ⁶H_{11/2}). Among these three transitions (⁴F_{9/2} → ⁶H_{13/2}) at 575 nm shows bright yellow emission intensity. In the present work, we have measured the lifetimes (τ_m) of yellow (575 nm) and blue (483 nm) emission transition with the excitation wavelength 482 nm. The energy level scheme for the emission process in Dy³⁺: glass with $\lambda_{\text{exi}} = 482$ nm is shown in Fig.9. The decay curve of the emission transition of 1.5 mol % of Dy³⁺: CdPbBAIF glass at 483 nm along with their life time is shown in the Fig.10. The decay curve is fitted to single exponential function as: $I = K \exp(-t/\tau)$ where 'K' is the constant and value of ' τ ' is decay time of Dy³⁺: CdPbBAIF glass. The obtained life time value is 0.48655 ms.

IV. CONCLUSION

In summary, it is concluded that, we have successfully developed highly transparent, stable and moisture resistant Sm^{3+} and Dy^{3+} : CdPbBAIF glasses. From XRD profiles, the glass amorphous nature has been studied. Vis-NIR absorption spectra of Sm^{3+} and Dy^{3+} : glasses have been measured and studied systematically. Emission spectra of Sm^{3+} and Dy^{3+} : CLBT glasses have been measured. From the emission spectra of these glasses luminescence properties have been studied. Intense reddish-orange and yellow colours are observed in Sm^{3+} and Dy^{3+} ions doped glasses respectively, when placed under an UV source. Based on the spectral results, we suggest that the Sm^{3+} and Dy^{3+} doped glasses are promising luminescent materials in the development of optical display systems.

V. ACKNOWLEDGMENT

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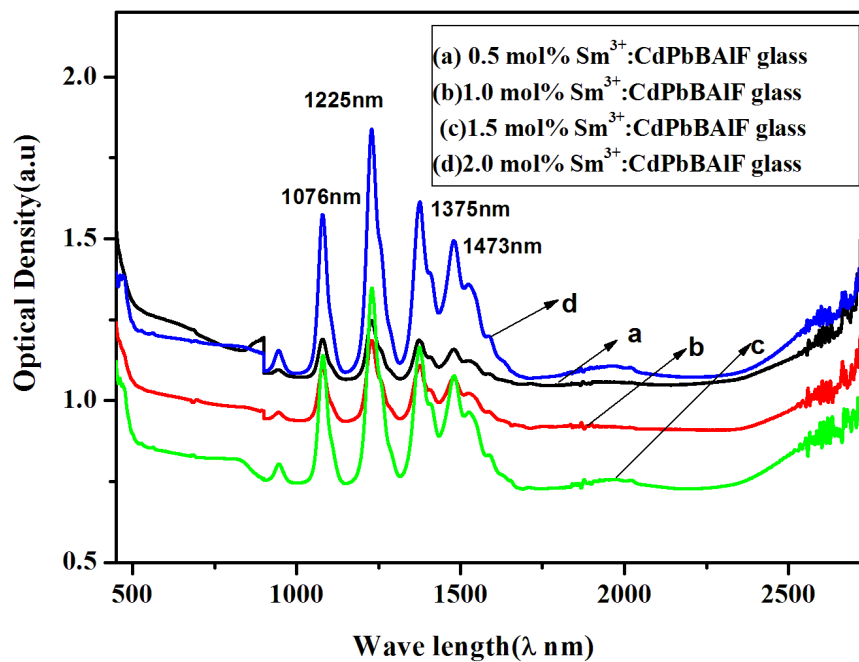


Fig.1. Vis-NIR absorption spectra of Sm³⁺: CdPbBAIF glasses

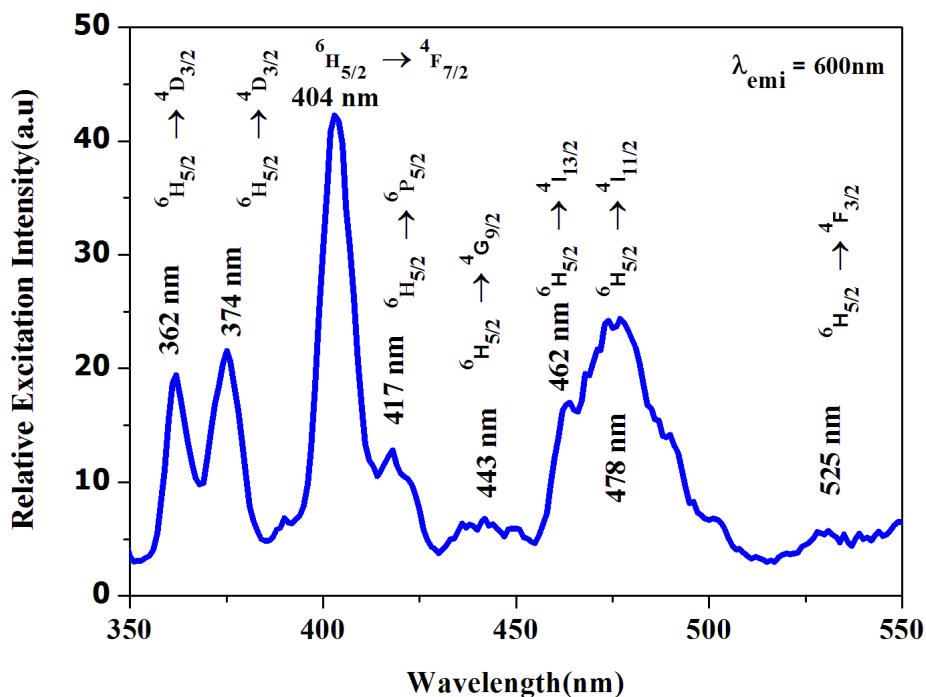


Fig.2. Excitation spectrum of Sm³⁺: CdPbBAIF glasses

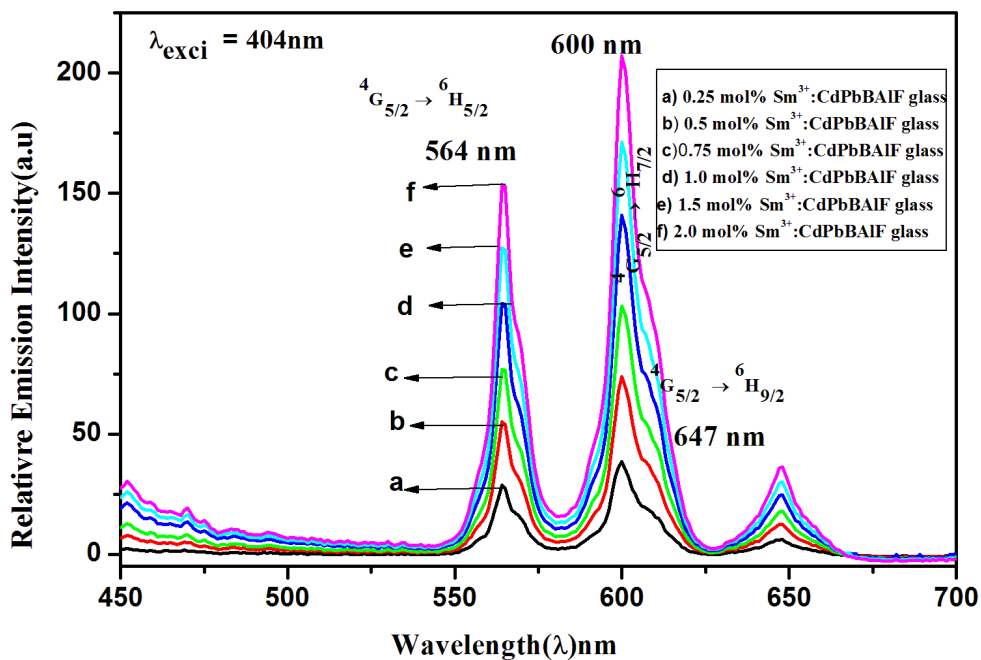


Fig. 3. Emission spectra of Sm³⁺: CdPbBAIF glasses

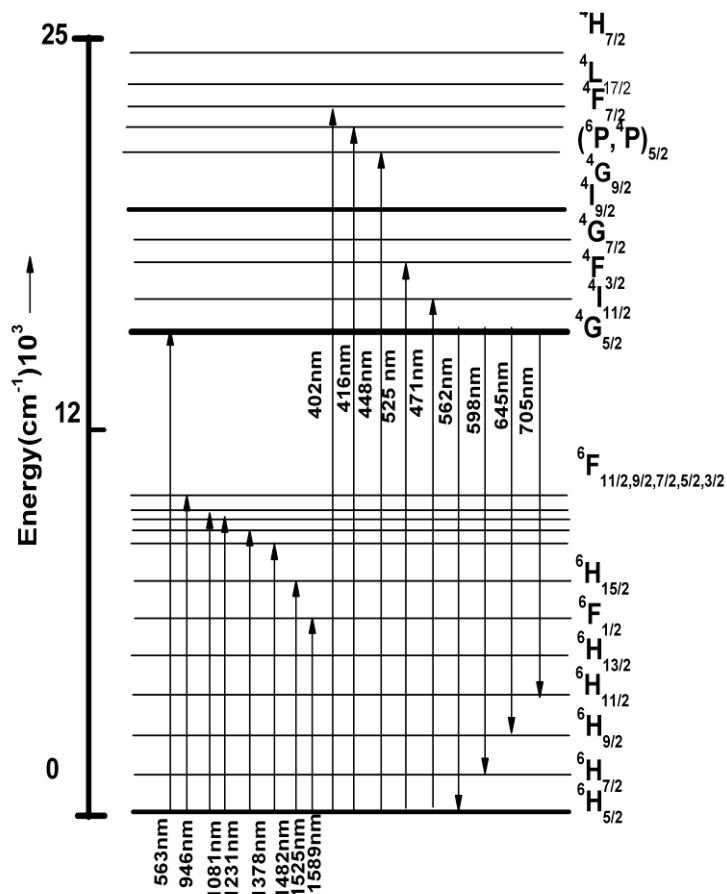


Fig. 4. Absorption, excitation and emission energy levels scheme of Sm³⁺: CdPbBAIF glasses

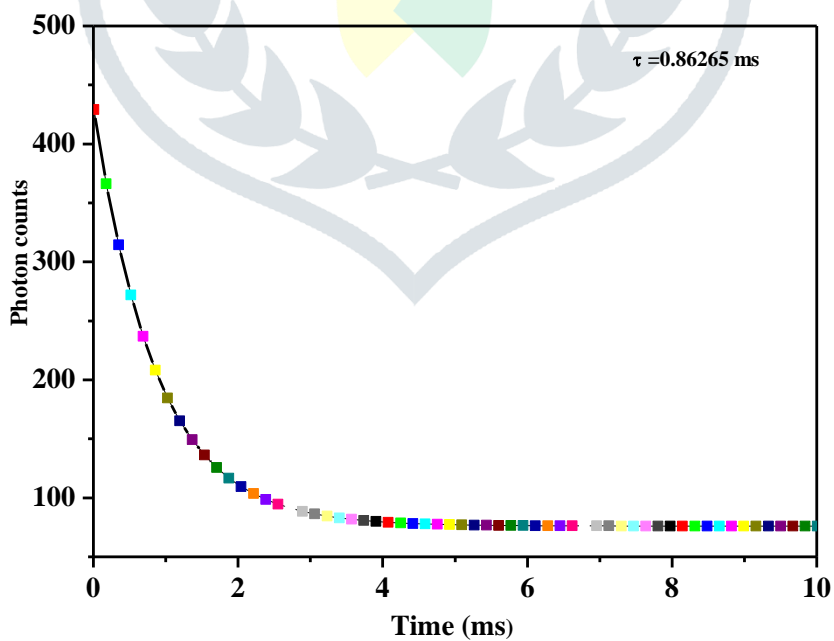


Fig.5. Decay curve of the emission transition of Sm³⁺: CdPbBAIF glass

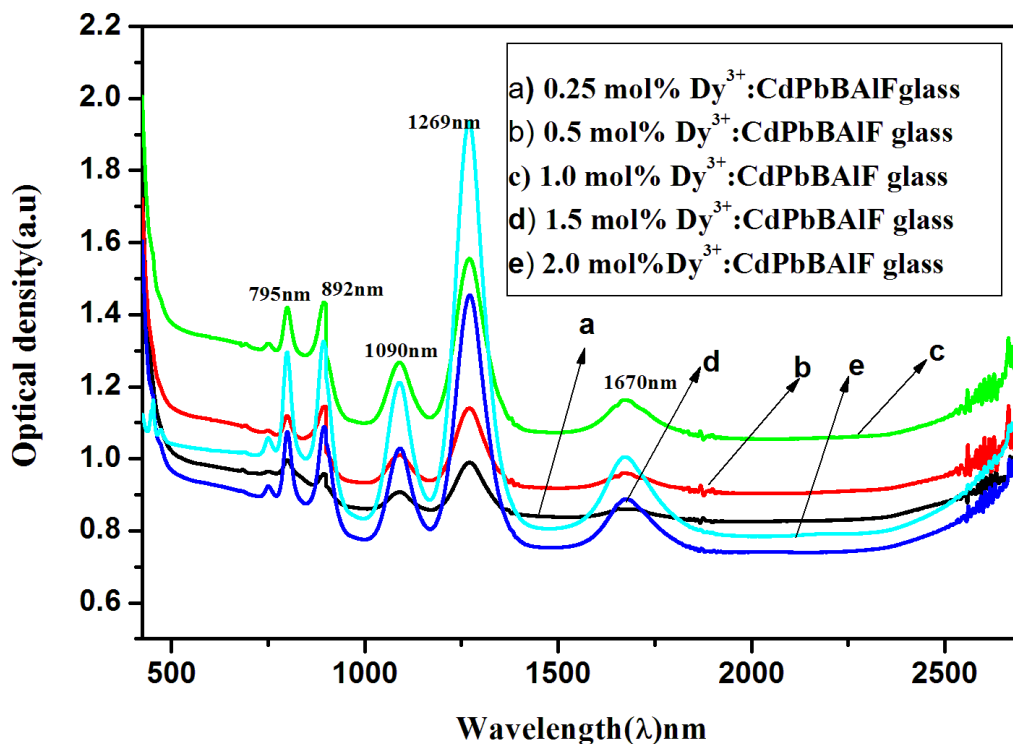


Fig. 6. Vis-NIR absorption spectrum of Dy³⁺: CdPbBAIF glasses

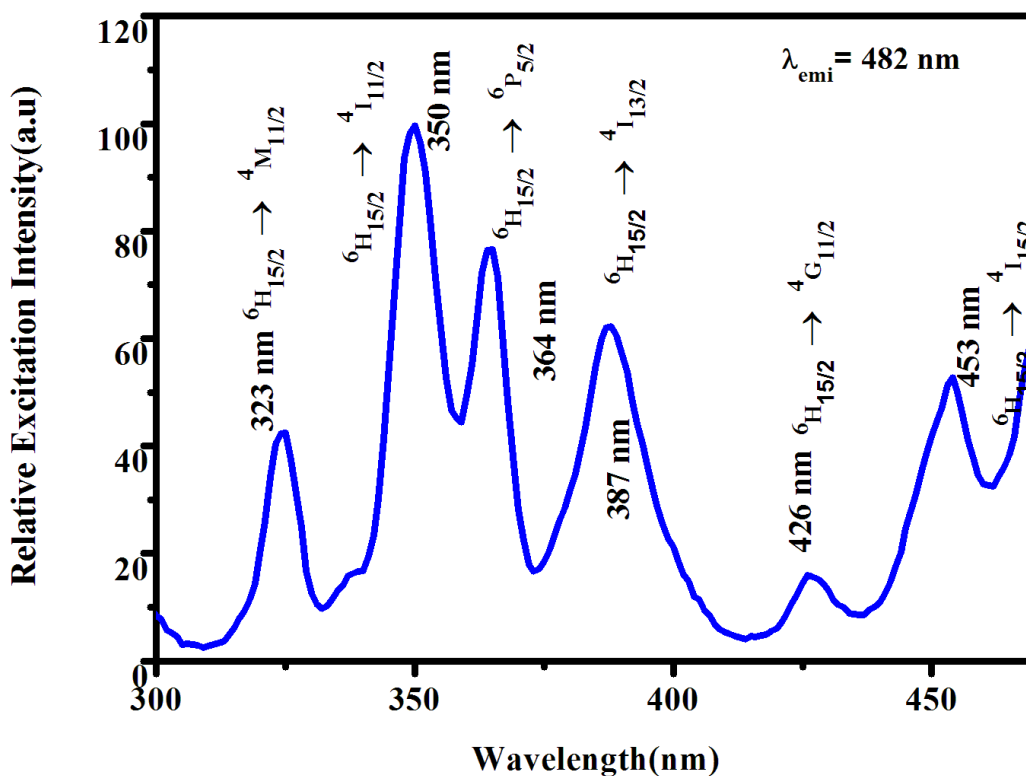


Fig. 7. Excitation spectrum of Dy³⁺: CdPbBAIF glasses

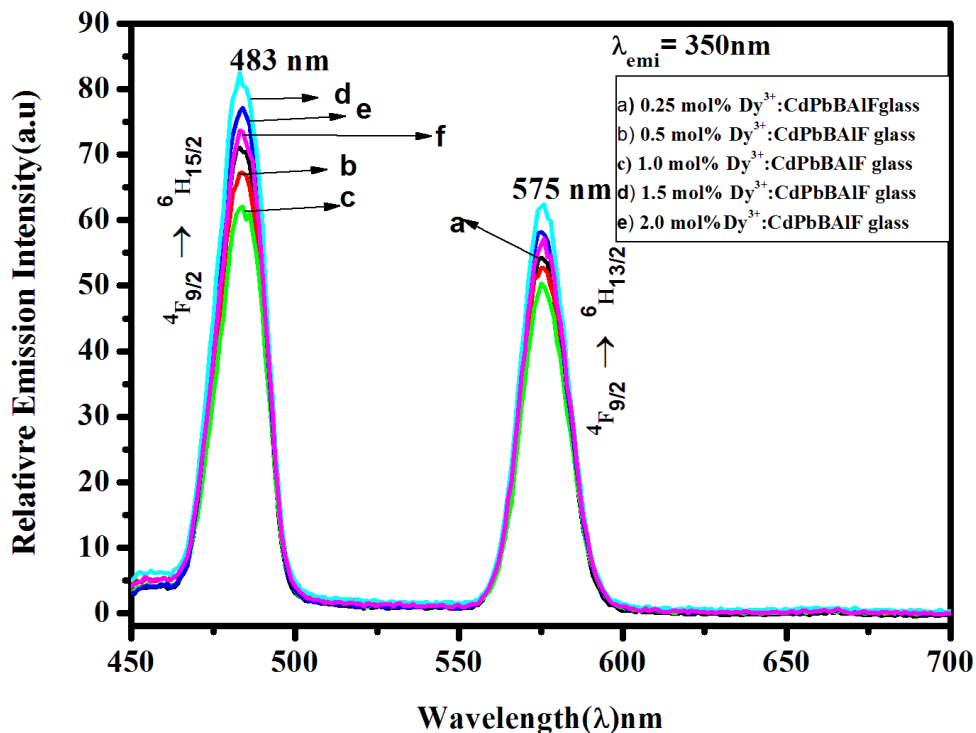


Fig. 8. Emission spectra of Dy³⁺: CdPbBAIF glasses

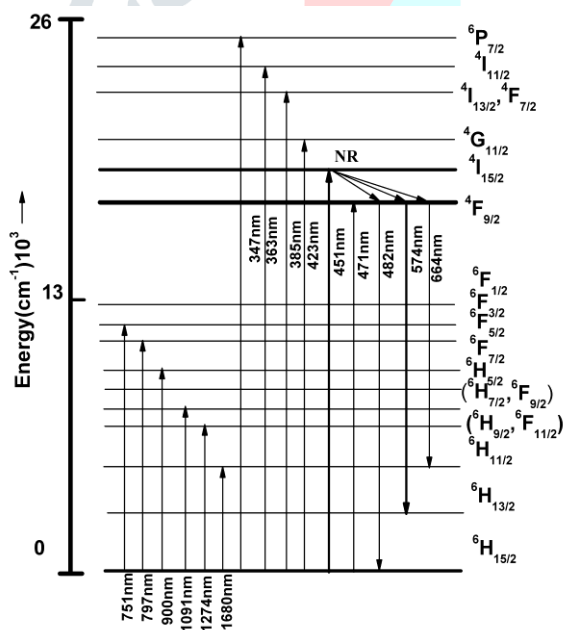


Fig.9. Absorption, excitation and emission energy levels scheme of Dy³⁺: CdPbBAIF glasses

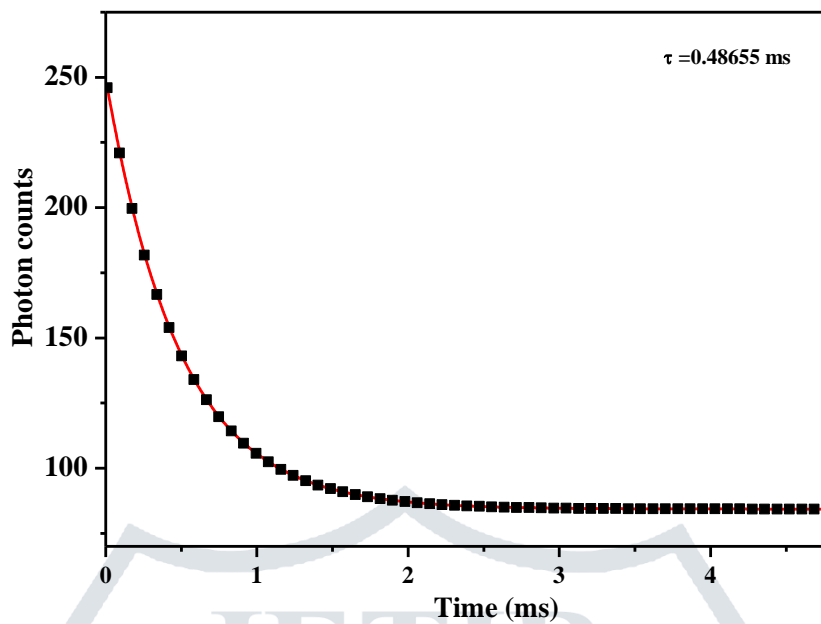


Fig.10. Decay curve of the emission transition of Dy³⁺: CdPbBAIF glass

